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Spectroscopy of van der Waals structures based on the transition metal dichalcogenide WS_2

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Received December 13, 2024
Revised April 3, 2025
Accepted April 8, 2025

The low-temperature photoluminescence and light reflection spectra of thin layers (down to monolayers) of WS_2 on oxidised silicon substrates were investigated. A rich interference structure was observed in the reflection spectra. By comparing the reflection spectra from the SiO_2/Si substrate and from WS_2 using the known refractive index, the thicknesses of these layers were determined. It was found that most of the lines in the reflection spectra are associated with the Si/SiO_2 layer. A series of lines previously attributed to the ground and excited states of the exciton were observed in the photoluminescence and reflection spectra from WS_2. It was established that these lines are associated with light interference near the exciton resonance in WS_2 at an energy of 2.15 eV.

Keywords: spectroscopy, transition metal dichalcogenides, excitons.

DOI: 10.61011/TPL.2025.07.61429.20224

The implementation of new microelectronic technologies is based on the study and identification of the fundamental properties of novel materials, especially those with reduced dimensionality. Classical computers use silicon components, which are currently approaching the pinnacle of their technological and physical development. One of the most promising lines of development of modern electronics is the transition to optical components.

It was demonstrated in numerous studies that the switching frequency of optical elements should be 2–3 orders of magnitude higher than that of silicon elements (at equal power consumption) [1]. The synthesis and study of new materials (in particular, low-dimensional systems) with optically controllable optical and electronic properties is one of the priorities of modern nanophotonics and nanoelectronics. Semiconductor nanocrystals of various shapes and sizes are of particular interest. In addition to such well-examined zero-dimensional semiconductor structures as quantum dots of various morphologies and compositions [2,3], a new type of semiconductor nanostructures is being studied extensively at present: two-dimensional layers of transition metal dichalcogenides [4,5].

The possibility of rearrangement of optical resonances, high exciton binding energies, and the feasibility of efficient energy transfer between resonances are the characteristic features of such nanosystems [6–8].

Van der Waals heterostructures [9], which are a combination of various 2D crystals of transition metal dichalcogenides [10,11] and a number of other materials [12], have been investigated extensively in recent years. Homostructures based on the same material are currently attracting more and more research attention. In the case of traditional semiconductors, they are formed from layers that have the same band structure but differ in doping. In contrast, 2D crystals offer another opportunity: the fabrication of homostructures from fragments containing different numbers of monolayers, since their band structure changes radically in transition from a monolayer to a bulk material or when the layers rotate relative to each other.

The present study is focused on van der Waals homostructures consisting of a bulk crystal and several isolated layers of atomic thickness on its surface. The structures were formed by exfoliation of flakes from high-quality WS_2 crystals. The same method was used in the study of samples based on MoS_2 [13]. Owing to weak binding of layers, the upper layers could separate slightly from the underlying ones during mechanical exfoliation. As a result, the interlayer distance for the upper layers could be larger than the one in bulk WS_2 (Fig. 1).

Reflection and photoluminescence (PL) spectra of van der Waals structures containing one or more WS_2 monolayers were studied experimentally. The structures were positioned on a silicon substrate with an approximate thickness of 0.5−1 mm. The substrate surface was oxidized to form a SiO_2 layer. A 530 nm laser was used to excite PL. A halogen lamp was the light source used for recording the reflection spectra. Micro-PL and reflection spectra were measured at $T = 10$ K with a confocal microscope with a spatial resolution on the order of 1 μm, dispersed in a spectrometer with a focal length of 0.5 m, and recorded with a CCD camera. The width of the spectrometer entrance slit was 0.1 mm.

Figure 2, *a* shows the PL spectrum of a sample containing several monoatomic WS_2 layers recorded in the region of the direct exciton transition at an excitation density of 6 W/cm^2. A broad (400 meV) PL band with a maximum at an energy close to 1.95 eV (dashed curve) is seen in the spectrum. This band is modulated by a set of narrower lines. A deep

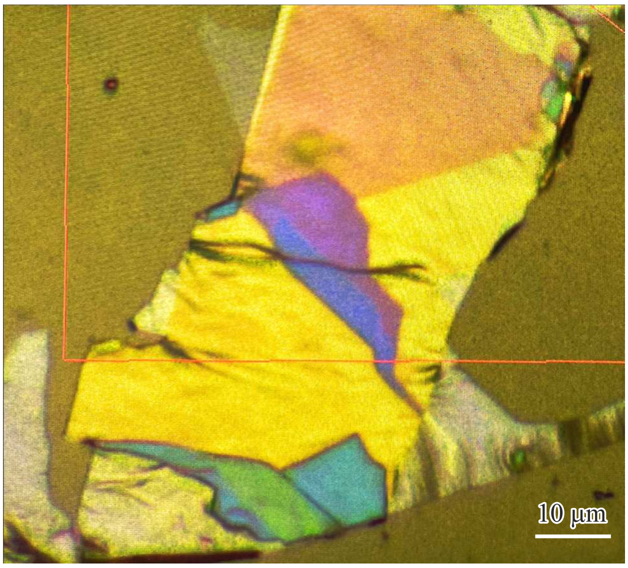

Figure 1. Photographic image of the surface of the WS_2 multilayer sample on an oxidized silicon substrate. Different colors represent different layer thickness values (blue-violet layers are thinner than yellow-orange ones). A color version of the figure is provided in the online version of the paper.

minimum of the PL signal, which drops almost to zero, is found at the long-wavelength edge of the band (at an energy of 1.9 eV). A series of narrow converging lines is seen beyond this minimum. In [13], the main peak at 1.9 eV was associated with the absorption of light in the ground state of an exciton, while the lines located at higher energies were attributed to excited („Rydberg" [14]) states of an exciton in the WS_2 monolayer. Here we challenge this interpretation. Having analyzed the energy position of these lines, we found that it depends on line number n as $E_0 - \beta/\sqrt{n}$, where E_0 is the energy to which these lines converge and β is a certain coefficient. If one associates the set of dips in the PL spectrum with exciton absorption of light by the surface WS_2 layers and the PL band itself with exciton emission from lower-lying bulk WS_2 (as in [15]), the coefficient of exciton absorption of light at an energy of 1.9 eV should be $\alpha \approx 10^7 - 10^8\,\text{cm}^{-1}$. This is three to four orders of magnitude higher than the typical values of the coefficient of exciton absorption of light in semiconductors.

The reflection spectra also reveal a rich interference structure of narrow reflection lines (Fig. 2, *b*). Three groups of lines may be distinguished in the spectrum.

1. A set of diverging interference lines is found in the region of 1.89–1.975 eV. The energy position of these lines is proportional to the square of the line number: $\propto n^2$ (Fig. 3, *a*). The amplitude of these lines also increases with line number.

2. A weakly converging interference structure, which matches the structure of converging lines in the PL spectrum, is seen in the region from 1.975 to 2.10 eV. The energy position of these lines is proportional to $E_0 - \beta/\sqrt{n}$, $E_0 = 2.15$ eV (Fig. 3, *b*). Their amplitude decreases.

3. A small-scale structure in the energy range from 1.975 to 2.025 eV modulates the interference structure mentioned in the previous paragraph (Fig. 3, *c*).

Spectra of reflection directly from the oxidized silicon substrate were also measured (Fig. 2, *b*). It turned out that the energy positions of certain interference features of the substrate reflection spectrum match the energy positions of features in the WS_2 sample spectrum. However (Fig. 4), they have opposite phases (maxima correspond to minima, and vice versa).

It is evident that the lines in the reflection spectrum in the region of 1.89–1.975 eV are of interference nature.

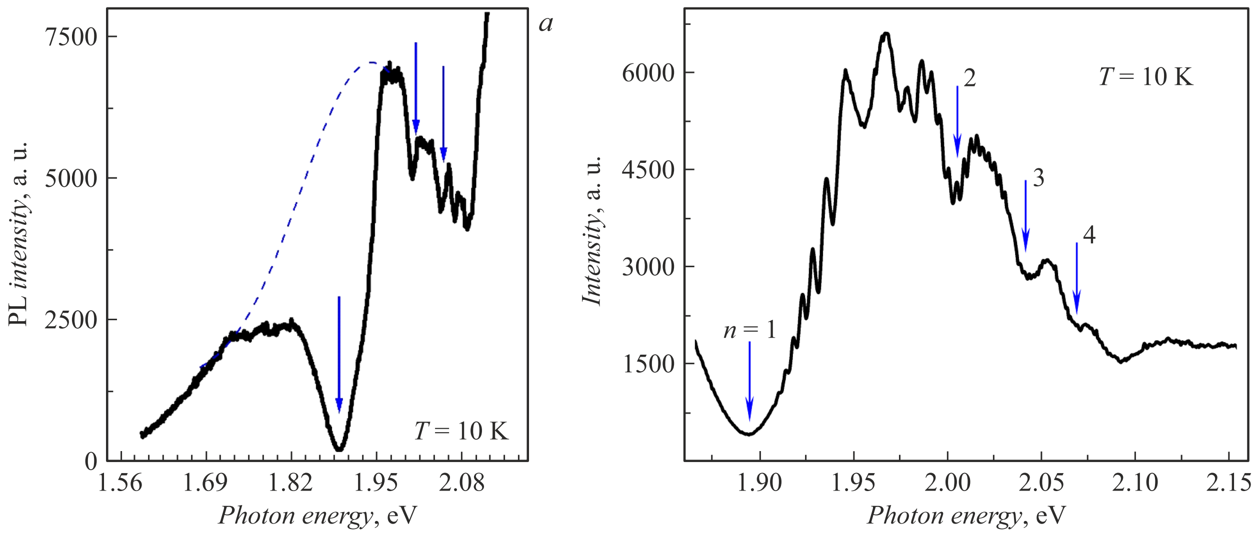

Figure 2. *a* — Photoluminescence spectrum in the region of direct exciton transitions of WS_2 multilayers on an oxidized silicon substrate. The dashed curve is the envelope of the FL signal modulated by interference. Arrows indicate interference features in WS_2. *b* — Reflection spectra measured in the region of 1.7–2.2 eV at a temperature of 10 K with normal incidence of light onto an oxidized silicon substrate. Arrows indicate interference features.

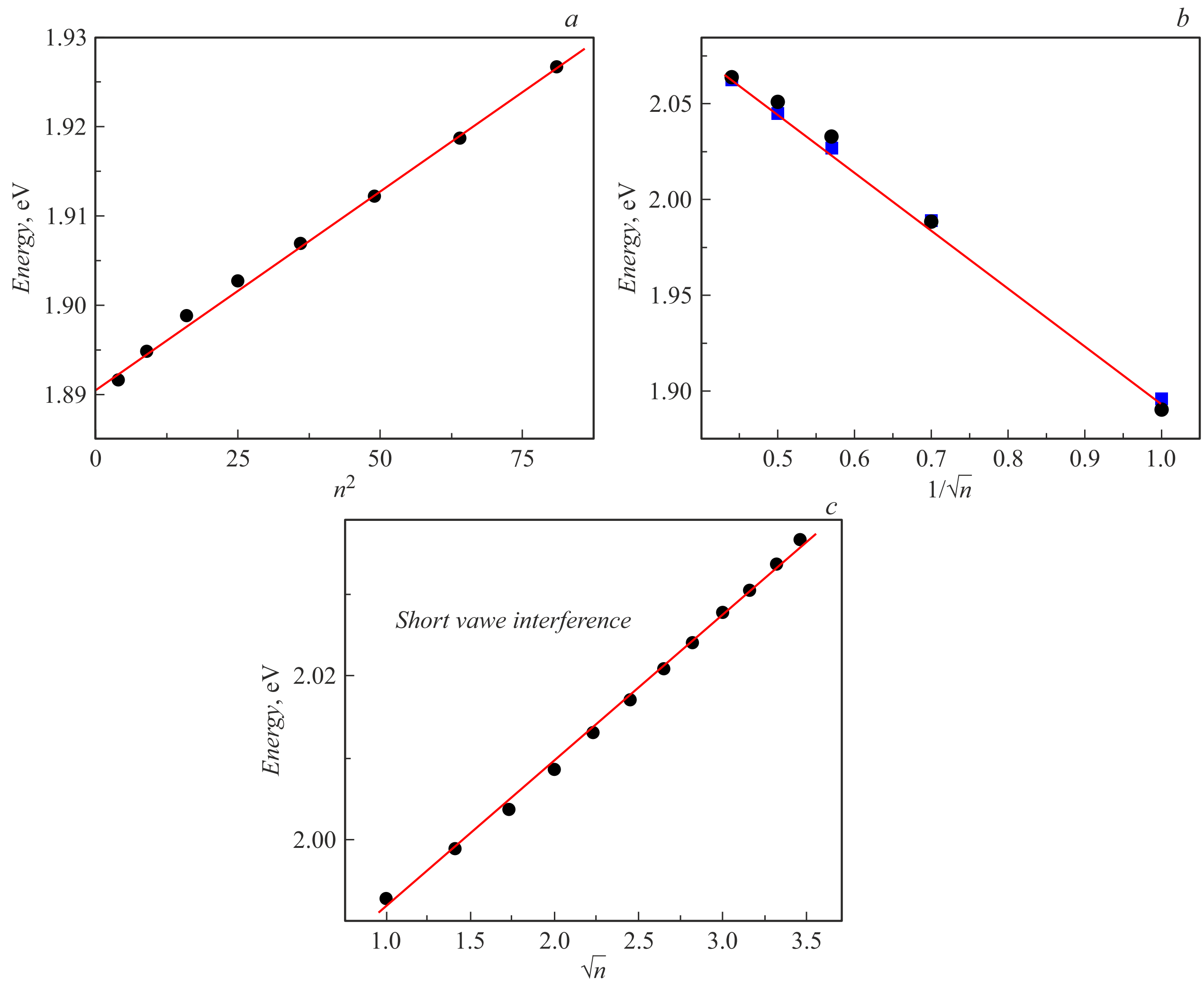

Figure 3. *a* — Dependence of the energy position of lines in the region of 1.89–1.93 eV in the reflection spectrum of WS_2 on a Si/SiO_2 substrate on the level number squared. *b* — Energy position of the lines of „Rydberg excitons“ as a function of the level number. Circles and squares represent the data obtained from the photoluminescence and reflection spectra, respectively. *c* — Dependence of the energy position of lines in the region of 1.99–2.04 eV in the reflection spectrum of WS_2 on a Si/SiO_2 substrate on the square root of the level number.

The dip in intensity, which drops almost to zero, at an energy of 1.890 eV is especially noticeable. Such a severe dip in reflection may only be attributed to interference under weak absorption (or even lack of it). This dip is not found in the substrate reflection spectrum, while all the other narrower lines in the spectra from the WS_2 sample and the substrate match in energy (Fig. 4). We associate the reflection maxima at the energies of 1.899 eV ($n = 1$), 1.989 eV ($n = 2$), 2.003 eV ($n = 3$), 2.045 eV ($n = 4$), and 2.069 eV ($n = 5$) with the effect of light interference in WS_2 layers. The considerable amplitude of these lines is indicative of weak absorption of WS_2 in this spectral region. The permittivity of WS_2 in this spectral region is $\varepsilon \approx 13$ [16–18]. The energy position of the indicated lines provides an opportunity to determine the effective WS_2 layer thickness, which is $\propto 0.34\,\mu$m.

The interference pattern in the substrate reflection spectra also allows us to estimate the thickness of Si/SiO_2. Setting the refraction index to $n = 1.7$, we find that the approximate thickness of the SiO_2 layer is 300 nm. It is noteworthy that the maxima in the spectrum of reflection from the WS_2 layers match the minima in the SiO_2/Si substrate reflection spectrum (Fig. 4). This indicates directly that the interference in question is associated specifically with the SiO_2/Si layer. Indeed, WS_2 has a higher refraction index than SiO_2, but the refraction index of SiO_2 is greater than the refraction index of vacuum. Therefore, when light is reflected at the SiO_2-WS_2 boundary and the SiO_2-vacuum boundary, the phase of reflected light has opposite signs. Subsequent passage of light through the WS_2 layer does not alter this relation.

The features in the PL and reflection spectra in the region of 1.89–2.10 eV are intriguing. These lines are obviously associated with light interference and cannot belong to the excited states of an exciton in WS_2 monolayers. The nature of the dependence indicates that this interference structure

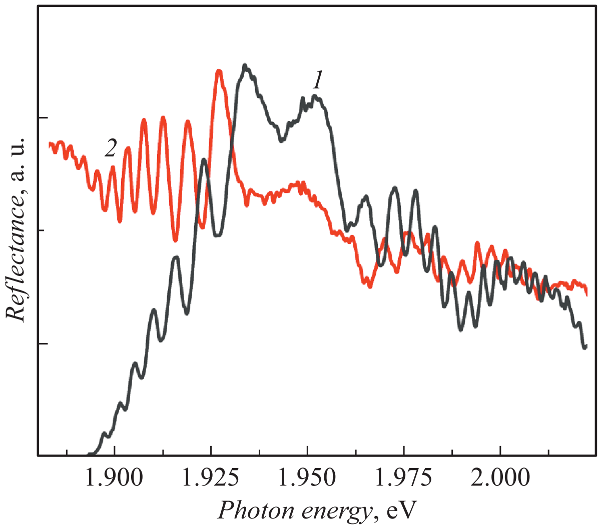

Figure 4. Comparison of spectra of reflection from the sample (*1*) and the substrate (*2*).

„converges“ to a certain resonant energy $E_0 \approx 2.15$ eV. This energy corresponds to the energy of a direct exciton in the WS_2 layer [19]. We believe that the broad PL band in the 1.6−2.1 eV region with a maximum at 2 eV (dashed curve in Fig. 2, *a*) corresponds to emission from porous silicon. Porous silicon is derived from ordinary silicon through oxidation (see [20] for details). Thus, a layer of porous Si should form in the substrate under the SiO_2 layer in the process of oxidation. The passage of this radiation through the WS_2 layer is accompanied by interference converging to the resonant energy of an exciton in the specified layer. As the energy increases, the attenuation of this wave becomes more pronounced, and the line amplitude decreases.

Thus, the photoluminescence and light reflection spectra of thin WS_2 layers (down to monolayers) on oxidized silicon substrates were investigated. A rich interference structure was found in the reflection spectra. The thicknesses of the SiO_2/Si substrate and WS_2 were measured by comparing the corresponding reflection spectra. It was found that the majority of lines in the reflection spectra are associated with the SiO_2 layer. A series of lines previously attributed to the ground and excited states of an exciton were observed in the photoluminescence and reflection spectra of WS_2. These lines converged to the exciton resonance at an energy of 2.15 eV. It was demonstrated that the indicated lines are associated with light interference in the WS_2 layer with a thickness of 0.34 μm.

Acknowledgments

The authors wish to thank M.O. Zhukova for providing the experimental equipment.

Funding

This study was supported by a grant from the Russian Science Foundation (No. 24-22-20059) and a grant from the St. Petersburg Science Foundation under agreement No. 24-22-20059 dated May 22, 2024.

Conflict of interest

The authors declare no conflict of interest.

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Translated by D.Safin